



Fe vacancies in FeOCl enhanced reactive oxygen species generation for photocatalytic elimination of emerging pollutants

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ABSTRACT

Reactive oxygen species (ROS) play an important role when using semiconductor photocatalysts in water remediation. Nonetheless, the insufficient conduction band potentials, as well as the limited mobility and quick recombination of charge carriers, often inhibit the ROS generation by many pristine photocatalysts. Here, we prepared FeOCl with tunable Fe-vacancy concentrations by using a NaCl-assisted thermal decomposition method. The defective FeOCl exhibited significantly higher rates of degradation and mineralization for organic pollutants compared to the non-defective FeOCl. This superior performance is attributed to the much faster superoxide (O₂^{•-}) and singlet oxygen (¹O₂) generation. Based on the experimental data and DFT simulations, Fe vacancies serve as electron trapping sites, leading to enhanced carrier lifetime and mobility, and can also reduce the conduction band potential of FeOCl, hence facilitating the formation of ROS. This study provides useful insights for developing cation-defected inorganic semiconductors and for improving the efficiency of O₂ activation in photocatalysis.

1. Introduction

Emerging organic pollutants, including endocrine disruptors, pharmaceutical and personal care products, and pesticides, have caused significant pollution in the aquatic environment worldwide [1–6]. This contamination has contributed substantially to the global water security issue to date [7,8]. The utilization of sunshine and molecular oxygen (O₂) by photocatalytic processes has long been considered an ideal approach for the elimination of POPs in wastewater [9,10]. When O₂ is activated by photocatalysts under sunlight irradiation, the reactive oxygen species (ROS) produced are capable of breaking down and even completely mineralizing most emerging pollutants [11]. Iron oxychloride (FeOCl) has recently been exploited as a potent photocatalyst for O₂ activation, owing to its narrow band gap energy (ca. 1.8 eV), tunable electronic characteristics, and minimal photocorrosion [12–14]. Nonetheless, these advantages are far from ideal for efficient photocatalytic water remediation applications [15]. Due to the quick electron-hole pair recombination, the carrier concentration on FeOCl surfaces is low [16]. Moreover, the dominating carriers in n-type FeOCl,

namely, the photogenerated electrons, have relatively low reducing activity. These factors cause FeOCl's activation of O₂ to generate ROS to be inefficient [17,18]. It remains highly desirable to improve the performance of FeOCl in photocatalytic O₂ activation for generation of ROS in order to further develop its application in water remediation.

Recently, multiple studies have documented the improvement in the effectiveness of ROS production in the FeOCl photocatalytic systems. The methods used mostly revolve around the construction of heterojunction composite systems [13,16,19–22]. Nevertheless, the efforts to improve the intrinsic photocatalytic capabilities of FeOCl are currently very scarce. Enhancing the intrinsic performance of photocatalysts is more conducive to realizing their full application potential. For other photocatalysts like TiO₂ and C₃N₄, multiple studies have shown that surface defects play a crucial role in controlling the spin nature, carrier concentration, and energy band structure, so that they can alter the inherent properties of photocatalytic materials and thereby increase the photocatalytic activity [23–27]. Therefore, we anticipate that defect engineering could be an useful approach to improve the inherent photocatalytic properties of FeOCl and enhance its performance in

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photocatalytic O_2 activation [28]. Among the various types of defects, cationic vacancies are a classic type of defect that plays a crucial role in photocatalytic processes [29]. Cationic vacancies can modulate the energy band structure by shifting the VB maxima upward and the CB minima downward without creating new intermediate states [30]. In addition, cationic vacancies are able to act as the transfer channels for carrier migration, thereby accelerating the charge carrier transfer and promoting the separation efficiency of photo-generated carriers [30,31]. The modulation of energy bands and electronic structures induced by cationic vacancies will be promising to improve the performance of FeOCl photocatalytic activation of O_2 . However, it is less explored relative to anionic defects such as O vacancies, due to the lack of facile approaches for preparing of cation-defected semiconductors and modulating of the concentration of the vacancies. This may be caused by the large formation energy [32]. To our knowledge, FeOCl with Fe vacancies has not been investigated. Further investigation is also required to understand the mechanism of the role of Fe vacancies in the photocatalytic activation of the O_2 reaction.

Herein, we have successfully realized the preparation of FeOCl with controllable Fe vacancy concentration using a facile method of NaCl-assisted thermal decomposition. Fe vacancies improved the charge separation and transport efficiency of FeOCl, and modulated the energy band structure of FeOCl, which facilitate the activation of O_2 to generate ROS, such as $O_2^{\cdot-}$ and 1O_2 . Benefit from the high ROS generation rate, FeOCl exhibited significantly higher rates of degradation (14 times higher) and mineralization for organic pollutants compared to the non-defective FeOCl. The degradation kinetics, pollutant scope, influence of coexisting ions and humic acid, and the effects of various water bodies were evaluated. Our results indicate that the Fe-defected FeOCl is promising in real water treatment processes. The microscopic structure, electronic structure, interfacial charge transfer, photogenerated charge carriers, and photo-response, were systematically studied by experimental techniques and DFT simulation. We found Fe vacancies serve as electron trapping sites, leading to enhanced carrier lifetime and mobility, and can also reduce the conduction band potential of FeOCl, hence facilitating the formation of ROS. Our findings provide useful insights for developing cation-defected inorganic semiconductors and for improving the efficiency of O_2 activation in photocatalysis.

2. Materials and methods

Supporting Information Text S1 provides a comprehensive description of chemicals, characterization instruments, and analytical methods.

2.1. Preparation procedures

The FeOCl sample with rich Fe vacancies were synthesized by a thermal decomposition method [33]. 5.0 g of $FeCl_3 \cdot 6H_2O$ and 0.15 g of NaCl were dissolved in 5 mL of deionized water in a glass beaker. The beaker was then heated in an oven at 70 °C for 15 h to remove most of the moisture from it. The above beaker was put in a pit furnace and heated at 240 °C for 90 min. The atmosphere was air and the rate of heating was 10 °C/min. After cooling to room temperature, the samples were crushed and rinsed with plenty of deionized water and acetone. The washed samples were dried at 60 °C overnight. FeOCl with rich Fe vacancies was collected after drying, named V_{Fe} -FeOCl.

The concentration of Fe vacancies in FeOCl can be controlled by adjusting the dosage of NaCl. The amount of NaCl was reduced to 0.03 g to prepare FeOCl with less Fe vacancies. This sample was used as a reference material, named V_{FeP} -FeOCl (V_{FeP} -FeOCl). Accordingly, pure FeOCl was obtained by the same preparation method without the addition of NaCl.

2.2. Photocatalytic degradation experiments

Bisphenol A (BPA) as a model pollutant was used to evaluate the

catalytic potency of the prepared samples for degradation of BPA (10 mg/L) under simulated AM-1.5 (1 SUN, 1000 W·m⁻²) solar irradiation. A xenon lamp (LSH-X500) was used as a simulated sunlight source, and the irradiated area was 6 cm². In a typical experiment of photocatalysis, 5 mg photocatalyst was added to 9 mL deionized water in a glass tube (outer diameter = 20 mm; volume = 50 mL). After ultrasonication of 3 min for dispersion, 1 mL of 100 ppm BPA solution was added into the above glass tube. Then, air was bubbled in the dark for 30 min to achieve adsorption and desorption equilibrium. At the specific time, 1 mL of reaction solution was taken and immediately quenched with ethanol, and the suspension was filtered through a 0.22 μm membrane filter for analysis. A similar experimental procedure was utilized to determine the degradation efficiency of the other pollutants such as 4-chlorophenol, nitrobenzene, chloramphenicol and acetaminophen.

2.3. Theoretical calculations

The Vienna abinitio simulation package (VASP) 6.1.0 was used to carry out all the DFT calculations [34]. The spin-polarized generalized gradient approximation (GGA) technique with the Perdew–Burke–Ernzerhof (PBE) functional with D3 dispersion correction was employed. [35,36]. The utilization of the projector augmented wave (PAW) method allowed for the depiction of the fundamental operations of the atoms, with the energy of the wavefunctions determined at 500 eV. The wavefunctions were in a state of complete relaxation until there was a shift in electronic energy and the alteration in eigenvalues was less than 10⁻⁵ eV. The structures were fully relaxed until the maximal force on each atom was less than 0.02 eV/Å. V_{Fe} -FeOCl was built from 3 × 3 × 1 FeOCl supercell. The 4 × 4 × 2 and 1 × 1 × 2 Monkhorst-Pack grids were used for FeOCl and V_{Fe} -FeOCl, respectively. The electronic levels were occupation by setting Gaussian smearing with a width of $\sigma = 0.1$ eV. The rotationally invariant DFT+U was employed to describe the local Coulomb interactions between 3d electrons. The values of U of 5.3 eV are used for Fe-3d orbitals.

3. Results and discussion

3.1. Structural characterizations

Fig. 1a depicts the NaCl-assisted thermal decomposition procedure for the preparation of FeOCl with Fe vacancies. It has been reported that during the thermal decomposition of $FeCl_3 \cdot 6H_2O$, Cl tend to be stripped as HCl and HClO, O tend to be stripped synchronously as HClO, leading to pure FeOCl with 1:1:1 at. ratio [37]. The addition of NaCl was found to be effective in controlling the atomic proportion of Fe, O, and Cl, promoting the formation of FeOCl with Fe vacancies. This is confirmed findings of thermogravimetric mass spectrometry (TG-MS) analysis (Fig. S1). The release of HClO decreases significantly, suggesting that the decomposition process retains more O. The addition of NaCl provided sufficient additional Cl. Consequently, excess Cl and O leads to the inadequate supply of Fe and formation of Fe vacancies in FeOCl [38,39]. To confirm the role of NaCl, we prepared two samples possessing different Fe vacancies concentrations, FeOCl with Fe vacancies (V_{Fe} -FeOCl) and FeOCl with less Fe vacancies (V_{FeP} -FeOCl) by controlling the amount of NaCl added. The loadings of Fe vacancies increase from FeOCl to V_{FeP} -FeOCl, and then to V_{Fe} -FeOCl as more and more NaCl was used.

X-ray diffraction (XRD) and Raman spectrum was used to analyze the phases of V_{Fe} -FeOCl, V_{FeP} -FeOCl and FeOCl. Fig. 1b shows all the XRD peaks of V_{Fe} -FeOCl are well indexed to the standard card of FeOCl (JCPDS no. 72-0619). According to the analysis of peak width at half maxima, the V_{Fe} -FeOCl material exhibits a little lower level of crystallinity compared to FeOCl (Table S1). In addition, there is no apparent shift in the peak position of the (010) facet in V_{FeP} -FeOCl and V_{Fe} -FeOCl, providing preliminary evidence that no Na⁺ was inserted into the FeOCl interlayer (Fig. S2) [40]. The non-detection of Na⁺ in V_{FeP} -FeOCl and V_{Fe} -FeOCl by ICP-MS further confirms this. As shown in Fig. S3a, the

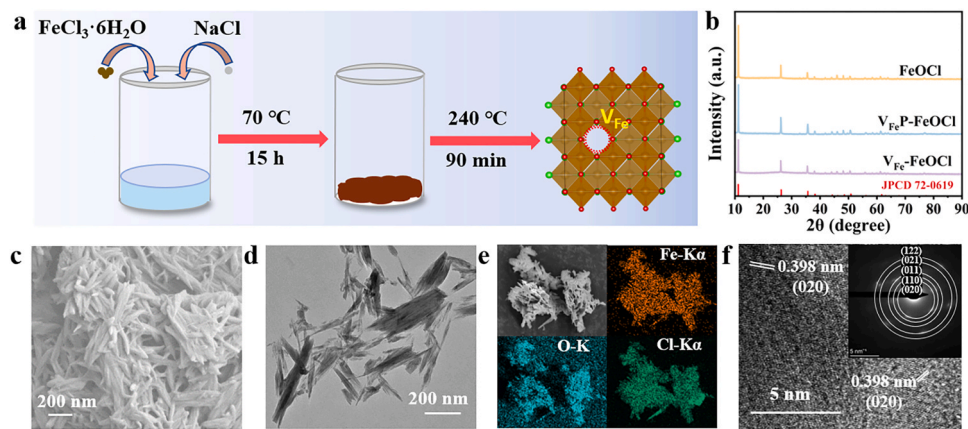


Fig. 1. (a) Schematic illustration for the synthesis of $\text{V}_{\text{Fe}}\text{-FeOCl}$. (b) XRD patterns of FeOCl, $\text{V}_{\text{Fe}}\text{P-FeOCl}$, and $\text{V}_{\text{Fe}}\text{-FeOCl}$. (c) SEM image of $\text{V}_{\text{Fe}}\text{-FeOCl}$. (d) TEM image of $\text{V}_{\text{Fe}}\text{-FeOCl}$. (e) HAADF-STEM and corresponding EDS mapping images of $\text{V}_{\text{Fe}}\text{-FeOCl}$. (f) HRTEM image (inset shows the SAED pattern).

Raman spectrum of pure FeOCl shows a peak at 214 cm^{-1} attributed to the Fe-Cl stretching mode, and the peaks at 280 and 394 cm^{-1} are attributed to the Fe-O stretching mode [41]. Significant negative shifts and broadening are observed in the Raman peaks of $\text{V}_{\text{Fe}}\text{P-FeOCl}$ and $\text{V}_{\text{Fe}}\text{-FeOCl}$, in comparison to FeOCl. The alteration in the long-range arrangements of the crystals may be the cause, consistent with the more Fe-defects in $\text{V}_{\text{Fe}}\text{P-FeOCl}$ and $\text{V}_{\text{Fe}}\text{-FeOCl}$ [42]. In the microstructures by SEM and TEM, pure FeOCl shows the typical laminated morphology (Fig. S4a and b). The added NaCl induces the formation of needle-like particles with smaller size (Fig. S4c and d). Ultimately, all the particles of $\text{V}_{\text{Fe}}\text{-FeOCl}$ show the spindle-like shape with lengths ranging $0.2\text{--}1.0\text{ }\mu\text{m}$ agglomerated by needle-like particles (Fig. 1c and d). The EDS mapping profiles on $\text{V}_{\text{Fe}}\text{-FeOCl}$ exhibit a uniform distribution of the elements Fe, O, and Cl (Fig. 1e). Furthermore, the SAED pattern confirms the crystal structure of $\text{V}_{\text{Fe}}\text{-FeOCl}$ (Fig. 1f). There, the lattice spacings of $\text{V}_{\text{Fe}}\text{-FeOCl}$ are consistent with the (020) and (110) planes of FeOCl [43,44]. The BET surface area of FeOCl and $\text{V}_{\text{Fe}}\text{-FeOCl}$ was calculated using N_2 absorption-desorption isotherm (Fig. S5). All the samples exhibit type IV isotherm [37]. $\text{V}_{\text{Fe}}\text{-FeOCl}$ ($22.1\text{ m}^2\cdot\text{g}^{-1}$) has a larger BET area than FeOCl ($7.3\text{ m}^2\cdot\text{g}^{-1}$).

Additional comprehensive characterizations were performed to further characterize the Fe-vacancies. In the electron paramagnetic resonance (EPR) spectra, $\text{V}_{\text{Fe}}\text{P-FeOCl}$ and $\text{V}_{\text{Fe}}\text{-FeOCl}$ display a similar signal at approximately $g = 2.002$ (Fig. 2a), which can be attributed to the electrons trapped in the iron vacancies [42,45]. $\text{V}_{\text{Fe}}\text{-FeOCl}$ has the highest signal intensity, indicating the highest loading of vacancies. The atomic contents of the samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). As the concentration of vacancies increases, the Fe contents in samples decrease significantly, and the Cl and O contents increase at the same time, suggesting that the predominant defect type is Fe vacancies (Fig. 2b and Table S2). And further using the variation of atomic ratios, the content of Fe vacancies in $\text{V}_{\text{Fe}}\text{P-FeOCl}$ and $\text{V}_{\text{Fe}}\text{-FeOCl}$ is estimated as 2.1% and 7.2% [42,46,47]. X-ray absorption fine structure spectroscopy (XAFS) was employed to analyze the coordination structures of Fe atoms in $\text{V}_{\text{Fe}}\text{-FeOCl}$ and FeOCl at an atomic level. The k-edge shifts in the direction of higher binding energy from FeOCl to $\text{V}_{\text{Fe}}\text{-FeOCl}$, indicating that the valence state of Fe increases (Fig. 2c) [48]. This coincides with the observations by using X-ray photoelectron spectroscopy (XPS; Fig. S3b and c). In the XPS spectra, a slight rise in binding energy is observed when comparing FeOCl to $\text{V}_{\text{Fe}}\text{-FeOCl}$, which corresponds to an increase of the average Fe valence from 2.50 to 2.64. Both the results of the XAFS and XPS spectra are consistent with the existence of cationic vacancies [49,50]. The R-space curve allows us to determine the information of the ligand atoms. The positions of the peaks indicate the bond lengths of the ligand atoms, and the intensities reflect the disorder of the

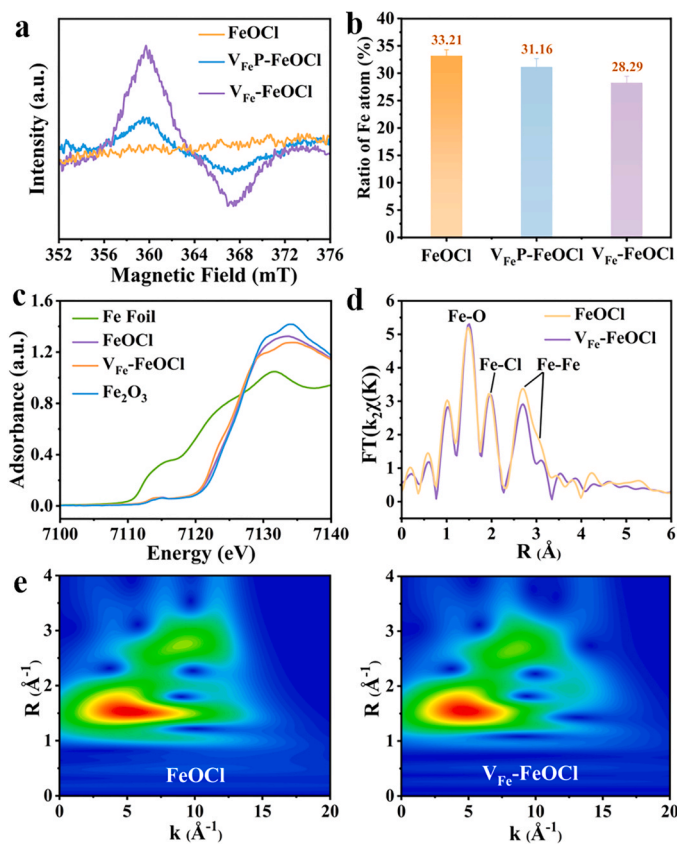


Fig. 2. (a) EPR spectra of FeOCl, $\text{V}_{\text{Fe}}\text{P-FeOCl}$, and $\text{V}_{\text{Fe}}\text{-FeOCl}$. (b) Fe atom ratios in FeOCl, $\text{V}_{\text{Fe}}\text{P-FeOCl}$, and $\text{V}_{\text{Fe}}\text{-FeOCl}$. (c) Fe K-edge XANES spectra of FeOCl, $\text{V}_{\text{Fe}}\text{-FeOCl}$, and Fe foil and Fe_2O_3 . (d) The Fe K-edge Fourier-transformed EXAFS spectra of FeOCl and $\text{V}_{\text{Fe}}\text{-FeOCl}$. (e) WT-EXAFS plots of FeOCl and $\text{V}_{\text{Fe}}\text{-FeOCl}$.

internal structure of the samples and the number of coordinating atoms. The Fe-O and Fe-Cl peaks marked in the spectrum of $\text{V}_{\text{Fe}}\text{-FeOCl}$ have similar intensity to those of FeOCl, while the Fe-Fe peak intensity is smaller due to the existence of Fe vacancies (Fig. 2d) [51]. We summarize the Fe coordination numbers obtained by fitting the spectra with EXAFS curve-fitting routines (Fig. S6). The formation of Fe vacancies in $\text{V}_{\text{Fe}}\text{-FeOCl}$ can also be reflected by a smaller coordination number (CN) of the Fe-Fe shells in Table S3 (CN $_{\text{Fe-Fe}} = 3.6$ and 1.7 for $\text{V}_{\text{Fe}}\text{-FeOCl}$ vs. CN $_{\text{Fe-Fe}} = 4$ and 2 for FeOCl), because of the absence of Fe atoms at the defect sites [52]. No O or Cl vacancies exist in $\text{V}_{\text{Fe}}\text{-FeOCl}$, because its CNs

of Fe-O shells and Fe-Cl shells are essentially the same as those of FeOCl, which are close to the theoretical value of 6 for the octahedral structure [43]. In line with the above results, the WT-EXAFS plots of FeOCl and V_{Fe} -FeOCl also confirm the exclusive existence of Fe-Fe and Fe-O coordination (Fig. 2e). To summarize, we successfully fabricated the V_{Fe} -FeOCl material rich in Fe vacancies by using a NaCl-assisted pyrolysis approach. This method also enables us to regulate the vacancy concentration.

3.2. The photocatalytic degradation performance

The photocatalytic degradation performances of V_{Fe} -FeOCl for organic pollutants in wastewater were investigated using BPA as the model persistent organic pollutant. The control studies indicate that adsorption is minimal, and the degradation process necessitates the presence of photocatalysts, light irradiation, and O_2 (Fig. 3a). Within 25 min, V_{Fe} -FeOCl degraded 100% of BPA, while pure FeOCl only degraded 20.9%. Moreover, V_{Fe} -FeOCl was more efficient than $V_{Fe}P$ -FeOCl, indicating the degradation efficiency of BPA increases with the loading of Fe-vacancy. The degradation kinetics could be modeled using the pseudo-first-order kinetic equation (Fig. S7) [53]. V_{Fe} -FeOCl has the largest rate constant (0.168 min^{-1}), which is 14 times that of FeOCl (0.012 min^{-1} ; Fig. 3b). By comparing the BPA degradation rate and first-order rate constants, V_{Fe} -FeOCl is outstanding compared to state-of-the-art photocatalysts (Table S4). We also investigated the potential of V_{Fe} -FeOCl to degrade BPA when exposed to real sunlight. To our delight, it has remarkable photocatalytic efficiency, with about 99.8% of BPA degraded in 100 min (Fig. S8). We detected the iron dissolution from the V_{Fe} -FeOCl system during the photocatalytic process and further investigated the effect of dissolved iron on BPA degradation (Fig. S9). The contribution of the homogenization reaction can be excluded due to the negligible degradation of BPA by dissolved iron.

According to HPLC-MS analyses, the degradation intermediates of BPA of the V_{Fe} -FeOCl system includes phenol, p-isopropenyl phenol, hydroquinone, 1-(3,4-dihydroxyphenyl)ethan-1-one, benzoquinone, 2-hydroxyacetic acid, and 2-hydroxypropionic acid (Table S5 and Fig. S10). The degradation pathways of BPA, dominated by 1O_2 and $O_2^{\bullet-}$, are presented below. In the first step, the β -scission of isopropyl between two phenyl groups in BPA leads to the degradation of BPA, which is triggered by ROS (1O_2 and $O_2^{\bullet-}$) and the production of phenol and p-isopropenyl phenol [54]. In the second step, the formed phenol and

p-isopropenyl phenol are further hydroxylated by 1O_2 to 1-(3,4-dihydroxyphenyl)ethan-1-one and finally to p-benzoquinone, which is easily decomposed [55]. In parallel to that, the previously formed aromatic intermediates are further decomposed to simple organic acids (2-hydroxyacetic acid, and 2-hydroxypropionic acid) by ring-opening reaction and then mineralized to CO_2 and H_2O by combined oxidation of 1O_2 and $O_2^{\bullet-}$. It is worth noting that all of these compounds are biodegradable [56].

Fig. 3c shows the temporal changes in the total organic carbon (TOC). After 20 min, when 97% of BPA had been degraded, the V_{Fe} -FeOCl system achieved a 38.2% reduction in TOC. The elimination of TOC increased steadily and ultimately reached a level of 62.8%. In contrast, by the FeOCl system, TOC removal was only 7.4% within 20 min, while hardly increased with prolonging the reaction time. Therefore, V_{Fe} -FeOCl not only degrades BPA in a higher rate, but also in a higher mineralization efficiency. Based on the successful application of V_{Fe} -FeOCl in the photocatalytic degradation and mineralization of BPA, the degradation of other organic pollutants was also examined. All the organic pollutants, including phenol (BP), 4-chlorophenol (4-CP), nitrobenzene (NBz), acetaminophen (APAP) and chloramphenicol (CAP), were completely photocatalytically degraded by V_{Fe} -FeOCl within a short reaction period (Fig. 3d). Reusability of photocatalysts is crucial in wastewater treatment. To investigate the reusability of V_{Fe} -FeOCl, we performed five consecutive cycles of BPA degradation experiments (Fig. 3e). The activity of V_{Fe} -FeOCl remained essentially unchanged. Meanwhile, SEM and XRD were used to characterize the morphology and structure of the recycled V_{Fe} -FeOCl after five runs. Fig. S11 shows that the structure and morphology of the catalysts maintained a high degree of consistency after five cycles of recycling, verifying the stability of V_{Fe} -FeOCl in water remediation.

During the wastewater treatment processes of organic pollutants, the photocatalytic activity of a photocatalyst can be affected by the pH of the wastewater, coexisting ions, dissolved organic matter, and other environmental factors. As shown in Fig. 3f, the acidic environment facilitated the degradation of BPA, while the alkaline environment slightly hindered its degradation. This is because the higher the acidity of the solution ($pH < 4.8$), the more positive the redox potential of $O_2/O_2^{\bullet-}$ is, which is more favorable for the conversion of O_2 to ROS [18]. Increasing the concentrations of ROS promotes the degradation of BPA. In the alkaline environments, excess OH^- induces charge repulsion thereby interfering with the participation of photogenerated electrons in

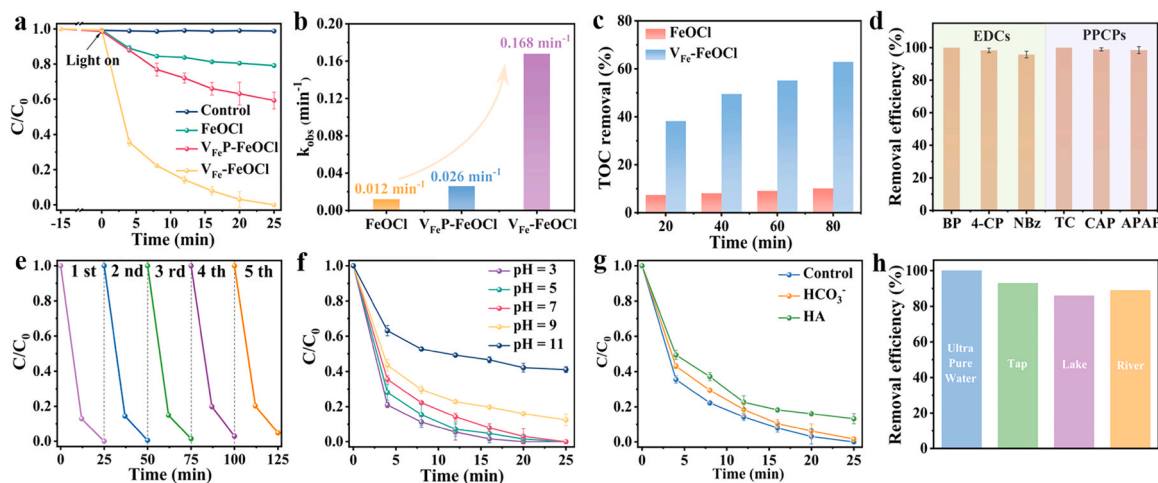


Fig. 3. (a) The degradation kinetics by the various systems under simulated solar light irradiation. Catalyst loading = 0.5 g/L and $[BPA]_0 = 10 \text{ mg/L}$. The – 15–0 min range shows the adsorption is negligible. (b) The first-order rate constants for FeOCl, $V_{Fe}P$ -FeOCl, and V_{Fe} -FeOCl. (c) TOC removal by FeOCl and V_{Fe} -FeOCl. (d) The degradation of six organic pollutants (44 μM) by V_{Fe} -FeOCl, including phenol (BP), 4-chlorophenol (4-CP), nitrobenzene (NBz), tetracycline (TC), chloramphenicol (CAP), and acetaminophen (APAP). (e) BPA degradation efficiency by V_{Fe} -FeOCl in five consecutive cycles. Effects of (f) pH, (g) HCO_3^- and HA on photocatalytic degradation of BPA (10 mg/L) by V_{Fe} -FeOCl. (h) The degradation efficiency of BPA by V_{Fe} -FeOCl photocatalysis within 30 min in different water bodies.

O₂ activation [57]. Nonetheless, V_{Fe}-FeOCl exhibited high degradation efficiency over a wide pH working window. Humic acid (HA) and HCO₃⁻ were used to explore the tolerance of V_{Fe}-FeOCl to dissolved organic matter and coexisting ions. Fig. 3g shows that HA and HCO₃⁻, even at high concentrations (5.0 mM), had negligible inhibitory effect on the BPA degradation. Therefore, the V_{Fe}-FeOCl photocatalyst exhibited high selectivity to the organic pollutants. Furthermore, the performance of V_{Fe}-FeOCl was also excellent in a variety of water sources (Fig. 3h). Overall, the performance of V_{Fe}-FeOCl was largely unaffected by various factors present in real water environments, indicating significant potential for use in wastewater treatment.

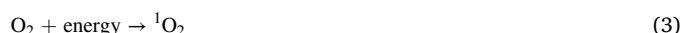
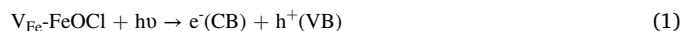
3.3. Efficient ROS generation

To investigate the ROS produced by the V_{Fe}-FeOCl photocatalyst, DMPO and TEMP were used as spin-trapping agents during the EPR tests. As shown in Fig. 4a, the sextet signals when using DMPO indicates that O₂^{•-} was produced, whereas in Fig. 4c, the triplet signals with 1:1:1 peak height when using TEMP indicates the formation of ¹O₂. Therefore, V_{Fe}-FeOCl generated both O₂^{•-} and ¹O₂ during the photocatalytic degradation of the organic pollutants. The signal strength of both O₂^{•-} and ¹O₂ in the V_{Fe}-FeOCl system is considerably higher than that of FeOCl. In addition, hydroxyl radicals (•OH) were also examined, and the absence of the characteristic quadruple peaks of •OH (intensity ratio of 1:2:2:1) confirmed the absence of •OH radical generation (Fig. S13). The precise quantity of the ROS produced was determined, as shown in Fig. 4b. The concentrations of ¹O₂ and O₂^{•-} in the V_{Fe}-FeOCl system reached 0.38 and 0.55 mM, respectively, within 30 min. These concentrations are 11.5 and 275 times greater than those detected in the FeOCl system, which are 0.033 and 0.002 mM, respectively. The enhanced production of the ROS by V_{Fe}-FeOCl demonstrates that the introduction of Fe vacancies enhances the photocatalytic activation of O₂ into ROS.

To further ascertain the roles of the ROS in the V_{Fe}-FeOCl photocatalytic system, we carried out the quenching experiments. As shown in Fig. 4d, tempol (O₂^{•-} scavenger) and FFA (¹O₂ scavenger) inhibited the degradation of BPA, leading to only 37.7% and 42.2% of BPA degradation after 25 min, respectively. Hence, O₂^{•-} and ¹O₂ are the major

reactive species responsible for the photocatalytic degradation of BPA. K₂Cr₂O₇ (electron scavenger) also substantially inhibited the degradation, due to cutting off the pathway of O₂ in formation of O₂^{•-}, further suggesting the important roles of O₂^{•-} and ¹O₂ in the degradation [14,57,58]. EDTA-2Na (hole scavenger) also inhibited the degradation of BPA to a certain extent, suggesting that holes are also involved in the degradation of BPA or ROS generation. In contrast, TBA and catalase did not induce inhibition of BPA degradation. Hence, •OH radicals, and H₂O₂ are not responsible for the degradation reaction. In all, the higher efficiency of V_{Fe}-FeOCl than FeOCl must be attributed to the more generation of ROS by the V_{Fe}-FeOCl system. Combined with quenching experiments and BPA degradation experiments in real water samples, the generation of ¹O₂ improves the degradation and mineralization rate of the system. Additionally, it enhances the anti-interference ability of the V_{Fe}-FeOCl/O₂ system, greatly increasing its potential for practical applications [59].

We also examined the origin of O₂^{•-} and ¹O₂ (Fig. S14). The degradation of BPA was significantly inhibited when the dissolved oxygen concentration was reduced using N₂. Correspondingly, the degradation efficiency of BPA by V_{Fe}-FeOCl was improved with the increase of dissolved O₂ concentration by bubbling O₂. These phenomena demonstrate that oxygen concentration is a major factor in the degradation of organic pollutants and V_{Fe}-FeOCl can effectively photoactivate oxygen to produce ROS for the degradation process [57]. Based on the above results, we can propose the process of O₂ activation to generate the ROS in this system. First, V_{Fe}-FeOCl generates electrons (e⁻) and holes (h⁺) under light irradiation (Eq. 1). The photo-generated electrons react with the O₂ molecules near the photocatalyst surfaces, resulting in the formation of O₂^{•-} (Eq. 2) [15]. ¹O₂ is formed through two routes: accepting energy from excited photocatalyst (Eq. 3) and oxidation of O₂^{•-} by h⁺ (Eq. 4) [11]. This can be demonstrated by ESR quenching experiments, which showed that both EDTA-2Na and Cr(VI) significantly inhibit the generation of ¹O₂ and the inhibition effect of Cr(VI) is more obvious (Fig. S15).



3.4. Structural roles for efficient ROS generation

The structure-activity relationship on the efficient generation of ROS by the Fe-defected FeOCl were studied. The UV-vis diffuse reflectance spectra (DRS) were utilized to analyze the photo-absorption properties. The DRS spectra in Fig. 5a demonstrate that Fe vacancies boost the photo-absorption of FeOCl. The absorption edge of V_{Fe}-FeOCl shows a considerable red-shift in comparison to FeOCl, which can be attributed to the presence of Fe vacancies [60]. The bandgap energies of FeOCl, V_{Fe}P-FeOCl, and V_{Fe}-FeOCl are approximated to be 1.81, 1.73 and 1.67 eV, respectively (Fig. 5b). The valence band (VB) potentials of the samples were determined by the XPS VB spectra. The VB potentials are 1.76, 1.50, and 1.33 eV vs. NHE for FeOCl, V_{Fe}P-FeOCl, and V_{Fe}-FeOCl, respectively (Fig. 5c). The conduction band (CB) potentials for FeOCl, V_{Fe}P-FeOCl, and V_{Fe}-FeOCl (Fig. 5d) are determined by these values and the bandgap values, which are -0.05, -0.23, and -0.34 eV (vs. NHE), respectively. It can be seen that the introduction of Fe vacancies exerts a substantial effect on the electronic structure of FeOCl. As a result, E_{CB} of V_{Fe}-FeOCl (-0.34 eV) becomes more negative compared to E(O₂/O₂^{•-}) which is -0.33 V, thus facilitating the formation of O₂^{•-} and the further oxidation of O₂^{•-} to ¹O₂ [18]. The effect of iron vacancies on the energy band of FeOCl was further explored using DFT calculations (Fig. 5e and

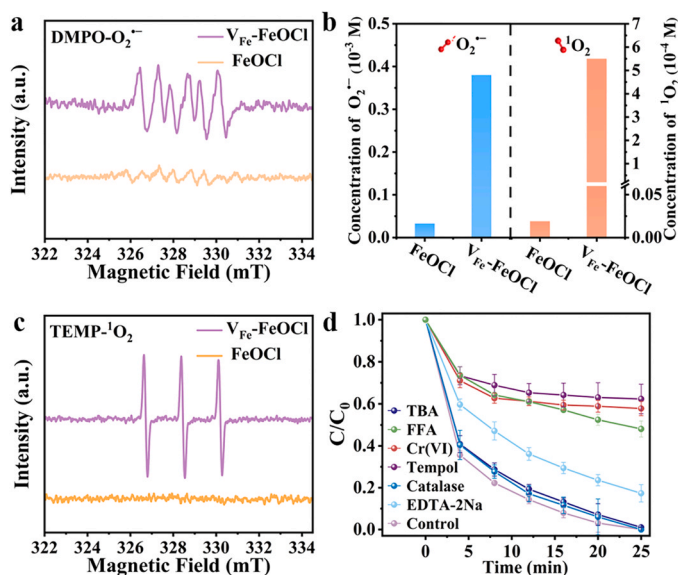


Fig. 4. ESR spectra of DMPO-trapped O₂^{•-} (a) and TEMP-trapped ¹O₂ (c). (b) The produced amount of O₂^{•-} and ¹O₂ during 30 min of photocatalytic reaction. (d) The effects of the scavengers in the photocatalytic degradation of BPA (10 mg/L) by V_{Fe}-FeOCl (0.5 g/L). The added concentrations are: 2 mM tertiary butanol (TBA), 200 units/mL catalase, 2 mM Tempol, 2 mM EDTA-2Na, 10 mM furfuralcohol (FFA), 1 mM K₂Cr₂O₇.

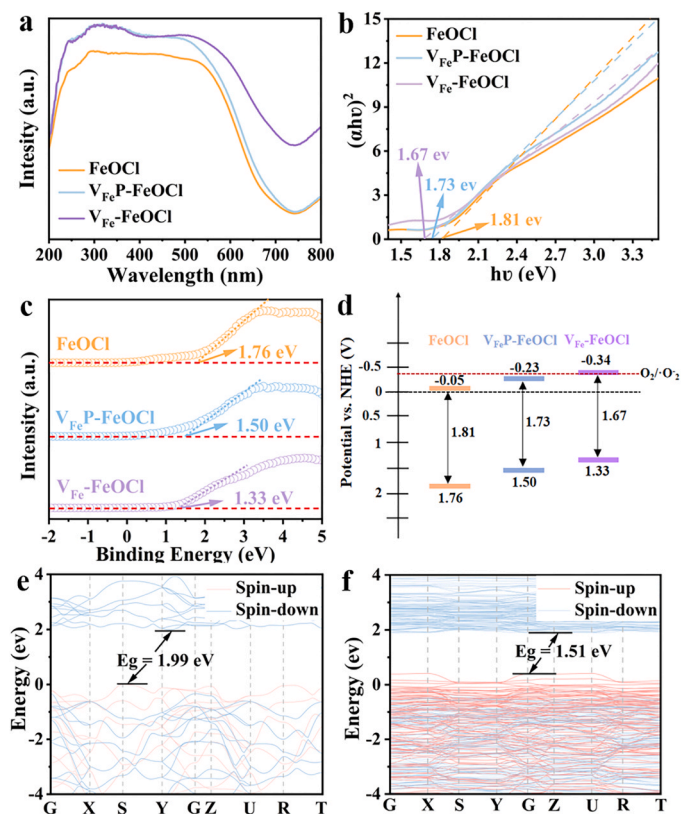


Fig. 5. (a) UV-vis diffuse reflectance spectra and (b) band-gap energy of different photocatalysts. (c) VB XPS spectra and (d) bandgap energies diagram of different photocatalysts. Calculated energy band structures of FeOCl (e) and VFe-FeOCl (f).

f). The calculated band gap of VFe-FeOCl (1.51 eV) is much smaller than that of FeOCl (1.99 eV), consistent with the experimental results.

Electrochemical impedance spectroscopy (EIS) was employed to investigate carrier transfer and interfacial reaction efficiency of the photocatalysts (Fig. 6a). For the samples with higher Fe-vacancy concentrations, the arc radii of the spectra are larger. The smaller arc radius of VFe-FeOCl reflects a lower resistance of charge transfer at the VFe-FeOCl/solvent interface in comparison to FeOCl, which is favorable enhancement of the charge transfer routes promoting generation of $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ [24,45]. Benefitting from these advantages, VFe-FeOCl generated notably stronger photocurrent than FeOCl and VFeP-FeOCl (Fig. 6b) [49]. The charge carrier density of a photocatalyst can be calculated by the slope of its Mott-Schottky curve (Fig. 6c). VFe-FeOCl has a higher charge carrier density than VFeP-FeOCl, followed by FeOCl. Obviously, the high charge carrier density in VFe-FeOCl benefits the interfacial charge transfer and energy transfer to generate $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$. [61]. The charge-separation efficiency and the lifetime of photogenerated charge carriers of the photocatalysts were assessed through photoluminescence (PL) and time-resolved PL spectra (Fig. 6d and Fig. S16). The spectra show a charge recombination signal at about 623 nm. As the concentration of Fe vacancies increases from FeOCl to VFeP-FeOCl and to VFe-FeOCl, the PL intensity decreases sharply, indicating that VFe-FeOCl has the most substantial carrier separation and transport efficiency. This conclusion is similarly confirmed by the time-resolved PL spectra, which shows the PL average lifetime follows the order $\text{FeOCl} < \text{VFeP-FeOCl} < \text{VFe-FeOCl}$. The better charge separation and longer lifetime of VFe-FeOCl are mainly due to the Fe vacancies that serve as separation centers, capturing more photo-generated electrons to promote the conversion of O_2 to ROS [23,62]. The density of states (DOS) functions of FeOCl and VFe-FeOCl were calculated (Fig. 6e and f). Compared to pure FeOCl, the introduction of iron vacancies leads to significant

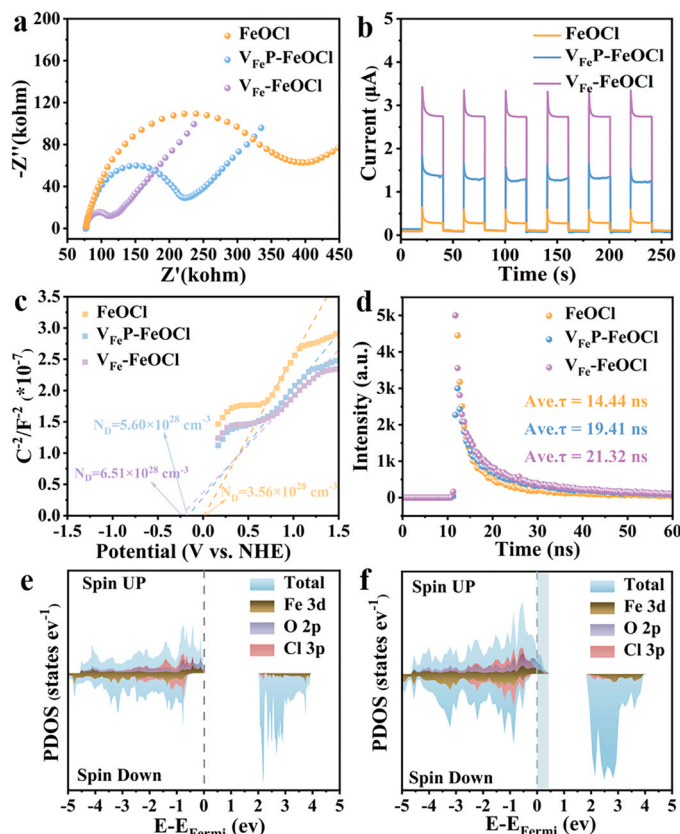


Fig. 6. (a) The electrochemical impedance spectra and (b) photocurrent response of different photocatalysts. (c) Mott-Schottky plots of different photocatalysts. (d) The nanosecond-level fluorescence decay spectra of different photocatalysts. Partial density of states (PDOS) spectra of FeOCl (e) and VFe-FeOCl (f).

electronic delocalization of neighboring atoms, resulting in a significant increase in the density of states of the spin-up component above the Fermi level, exhibiting typical half-metallicity characteristics [52,63]. This leads to a significant improvement in the conductivity of VFe-FeOCl compared to FeOCl, which boosts carrier mobility and enhances the O_2 activation process [64]. The calculated results are in excellent agreement with the electrochemical impedance spectra and photocurrent measurements.

Taken together, the boosted formation of $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ is responsible for the enhanced photocatalytic degradation and mineralization of the persistent organic pollutants by the Fe-vacancy containing photocatalysts, specifically, VFe-FeOCl. The enhanced generation of $\text{O}_2^{\bullet-}$ and $^1\text{O}_2$ is attributable to three main factors: the modulated energy band, enhanced charge separation, and accelerated dynamics of interfacial

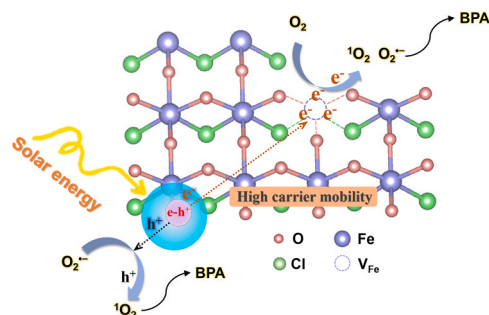


Fig. 7. Mechanism of Fe vacancy-enhanced O_2 activation for efficient pollutant degradation.

carrier transfer (Fig. 7). First, Fe vacancies modulate the electronic structure, leading CB position to become more negative than $O_2/O_2^{\bullet-}$, which is a prerequisite for the reduction of O_2 to $O_2^{\bullet-}$ and the oxidation of $O_2^{\bullet-}$ to 1O_2 . Fe vacancies have induced significant electron delocalization and improved the conductivity of the material, which boosts carrier transport. In addition, Fe vacancies can act as electron trapping centers to prolong the carrier lifetime. Efficient carrier mobility and separation greatly increase the carrier's concentration on the surface and contribute to the generation of $O_2^{\bullet-}$ and 1O_2 by charge and energy transfer. Therefore, the abundant Fe vacancies on the surfaces of V_{Fe} -FeOCl optimally optimize the key process in photocatalytic O_2 activation, which greatly improves the yields of $O_2^{\bullet-}$ and 1O_2 and realizes the efficient photocatalytic degradation of pollutants.

4. Conclusion

We have synthesized a FeOCl photocatalyst rich in Fe vacancies (V_{Fe} -FeOCl) for efficient photocatalytic degradation of emerging pollutants via a facile method, and explored in detail the mechanism by which Fe vacancies enhance the catalytic effect. The concentration of the Fe vacancies was facily controlled using a NaCl-assisted thermal decomposition approach. V_{Fe} -FeOCl exhibited superior performance compared to FeOCl, in terms of both reaction rate and mineralization rate, in the photocatalytic degradation of a variety of emerging pollutants, such as BPA. It is recyclable. It also showed great tolerance to a variety of environmental perturbations including coexisting inorganic ions and dissolved organic matter, pH change, and various water sources. The reactive oxygen species $O_2^{\bullet-}$ and 1O_2 are responsible for eliminating the pollutants, and their increased production on V_{Fe} -FeOCl leads to faster deterioration and more complete mineralization. We have analyzed in detail the mechanism of the enhanced photocatalytic performance of Fe vacancies by comprehensively characterizing their structure, electronic structure, photogenerated charge separation, and interfacial carrier transfer properties. It was found that Fe vacancies serve to modulate the electronic structure of V_{Fe} -FeOCl, resulting in a more negative CB potential. Furthermore, Fe vacancies enhance carriers separation and migration efficiency by acting as carrier trapping centers. This leads to V_{Fe} -FeOCl with higher carrier concentration, which greatly improves the reaction efficiency with O_2 and is more conducive to the efficient generation of ROS for pollutants degradation. Our results can be developed as a general method for the controlled synthesis of photocatalysts with cationic vacancies, as well as an inspiration for more effective utilization of O_2 and sunlight in the degradation of emerging pollutants.

CRediT authorship contribution statement

Zixuan Nie: Writing – original draft, Investigation, Data curation. **Chengji Sui:** Investigation. **Xiaobin Xie:** Investigation. **Shou-Qing Ni:** Funding acquisition. **Lingshuai Kong:** Investigation, Funding acquisition. **Yifeng Wang:** Investigation, Data curation. **Jinhua Zhan:** Project administration, Investigation, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2024.123819.

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